

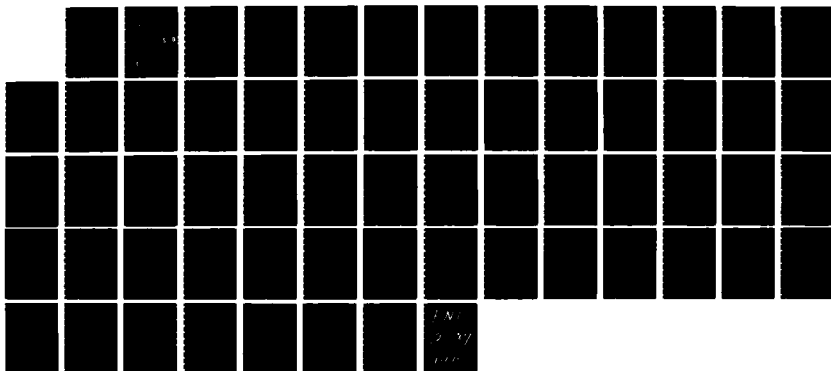
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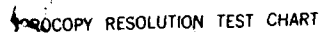
AN INTRODUCTION TO NAVY CORROSION PROBLEMS A GUIDELINE
FOR DESIGNERS AND (U) NAVAL SURFACE WEAPONS CENTER
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**AN INTRODUCTION TO NAVY CORROSION
PROBLEMS. A GUIDELINE FOR DESIGNERS AND
ENGINEERS OF NAVAL ORDNANCE AND HARDWARE.**

BY J. F. McINTYRE

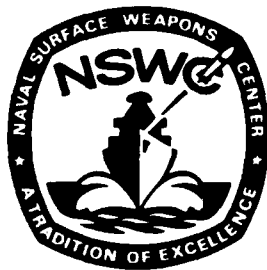
RESEARCH AND TECHNOLOGY DEPARTMENT

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FOREWORD

Corrosion failures of critical structures or weapons systems to the fleet are costly, not only in terms of dollars lost but more importantly the potential compromise of the safety of its crew. Therefore, the importance of placing more emphasis on preliminary corrosion studies during the design stages of new ships, vehicles, or ordnance needs no justification. This preliminary report represents a review of the nature of corrosion, a description of the most insidious forms of corrosion, and the experimental approaches necessary to study these problems which are critical to the design of new naval ordnance and hardware; for example, the corrosion problem areas associated with the design of a new generation of weapons/cargo elevator platforms is considered. Based on the introductory nature of this report it is hoped that important problem areas are highlighted and that cited literature will provide a starting point for designers and/or engineers concerned with the influence of corrosion on the structural integrity of their finished product.

Approved by:

Jack R. Dixon
 JACK R. DIXON, Head
 Materials Division

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CHAPTER 1

INTRODUCTION

Corrosion can be defined as the interaction of a metal with its environment. The reaction products can take the form of solids, gases, or liquids, each of which affects the performance and integrity of the metal.

Comprehensive research conducted to understand the nature of the corrosion process in order to prevent premature structural failure needs no justification. For example, it has been estimated that the nation's corrosion bill amounts to annual expenditure of approximately \$165 billion, or about 4% of the Gross National Product. The cost of corrosion to the federal government has been estimated at \$19 billion per annum. This expenditure includes replacement of failed parts, surface preparation and painting of metals, and the development and testing of expensive alloys and other materials. The federal government annually spends approximately \$8 billion to combat corrosion. For obvious reasons, the U.S. Navy requires a continuous source of funds and resources to control the corrosion problems faced by their fleet.

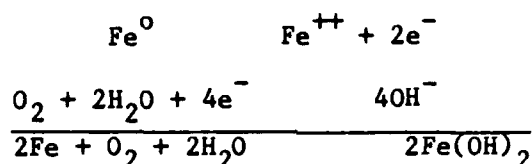
Design, construction, and deployment of Naval ordnance, from inception to delivery, requires an understanding of inherent corrosion problems and recognition of the consequences of premature failure. An understanding of these problem areas should assist in the selection of materials and aid in design modifications as needed for a given application. Most important, preliminary corrosion studies will ideally be able to predict the reliability and lifetime of operation of the ordnance in question. In addition, a practical design provides for cost-effective serviceability that includes easy methods of protective care and reasonable ease of repair and replacement of failed parts.

This report will introduce and discuss some of the corrosion problem areas that may be inherent in the design of any new Naval structure and ordnance; of particular interest is the nature of potential corrosion problems that pertain to the design and construction of a new generation of lightweight weapons elevator platforms. A general overview of corrosion will be presented; environmental effects and typical failure modes of corrosion pertinent to this project will also be addressed.

CHAPTER 2

NATURE OF CORROSION

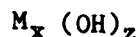
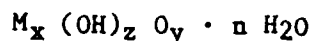
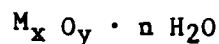
The corrosion of metals can be described as a stepwise interaction of events involving chemical, electrical, and physical processes occurring at the interface between a metal and its environment. Common to all corrosion mechanisms is the occurrence of two distinct reactions involving oxidation and reduction processes. In general, these reactions take place at specific anodic and cathodic sites on the metal surface. A metal atom is oxidized, at anodic sites, to metal ions with a liberation of electrons. These electrons migrate, i.e., electrical interaction, to cathodic sites, where they are consumed by the species being reduced. For example, the corrosion of iron in neutral aerated aqueous solutions can be represented by the following simple reaction scheme:



A subsequent chemical reaction occurs because the newly formed Fe^{++} ions have a strong propensity to recombine with oxygen and/or water to form oxides, hydroxides, and oxy-hydroxy compounds. In fact, for most metal oxides the free energy of formation is negative and in the presence of oxygen the oxide of a metal is thermodynamically more stable. In the absence of an aqueous environment, most metals spontaneously react with air to form an oxidized metal surface with a thickness of 10-30 Å. Many oxides provide a natural barrier to corrosive attack in a large number of environments; for example, the excellent corrosion resistance of aluminum can be attributed to its inherently adherent and chemically stable oxide.

The transformation from metal atoms to metal ions constitutes a physical change in the metal itself; in addition, the subsequent formation of an oxide, hydroxide, or oxy-hydroxy compound represents a physical alteration of the metallic state. In summary, an electrical reaction occurs involving a release and capture of electrons during reaction at anodic and cathodic sites, respectively. This is followed by a chemical reaction involving the metal ions and the immediate environment; as a consequence, physical changes take place, causing a permanent change in the metal surface state.

Corrosion products can be represented by the following generic designations:



where M represents the metal, x, y, and z are the stoichiometric amount of M, O, and OH respectively, and n is the number of water molecules of hydration. Each of these compounds is unique in its chemical reactivities. Their chemical identities can be characterized by analytical techniques such as Raman, infrared, and X-ray diffraction spectroscopies. In many cases, a strongly adherent nonporous oxide is produced that provides protection to the underlying metal surface, significantly reducing the corrosion rate. However, many oxides are weakly adherent and porous and provide little or no protection to the metal; thus corrosion proceeds unhindered. Occasionally a corrosion product may actually exacerbate the corrosion process, causing severe attack and rapid weight loss.

Manifestations of corrosion follow a number of different reaction pathways, each producing a variety of deleterious effects. A common type of attack is uniform corrosion, where the metal corrodes evenly and the surface is generally covered by a layer of corrosion products. Uniform attack occurs because the anodic and cathodic sites are constantly interchanging, i.e., no preferential areas are attacked. The rusting of iron in humid environments and the tarnishing of copper and silver in sulfur environments are among the more familiar examples of uniform corrosion.

A particularly insidious form of corrosion involves localized attack of the metal. Pitting corrosion and crevice corrosion are the most common forms of localized attack. Localized corrosion occurs at specific sites on the metal surface and, most often, the corrosion rate is greatly accelerated in comparison to other sections of exposed metal. The metal weight loss may be minimal; however, critical areas of a structure are often breached. For example, perforations of storage vessels such as those employed to store chemicals and gasoline (fuels) can be extremely detrimental to the environment, not to mention, the obvious waste of valuable resources. Although pitting corrosion may not significantly thin the metal, a large number of deep pits may weaken the substructure, often causing catastrophic and sudden failure, i.e., providing initiation sites for stress corrosion or fatigue cracks. Crevice corrosion is exactly what the name implies, corrosion occurring in a crevice, an area shielded from the bulk environment usually restricting the flow of oxygen and other reactants; in most cases, a region of high acidity develops, causing rapid attack within the crevice. Typically, potential crevice sites are inherent in the design and can be located under gaskets, washers, lap joints, bolts, and rivets; in addition, crevices may develop beneath surface deposits, e.g., bacterial fouling and corrosion products.

Caution must be exercised when two metals with different electrochemical reactivities are physically joined, since a potentially dangerous situation may soon develop. Corrosion involving dissimilar metals in contact is known as

galvanic or bimetallic corrosion. This type of corrosion is especially serious when aluminum is one of the coupled metals. Aluminum and its alloys are highly active according to the standard reduction potential (SRP) series. (See Table 1.) The SRP tables can be used as a guide to help predict a metal's corrosion tendency. Active metals, with more negative potentials, have higher tendencies to corrode at faster rates than do noble metals such as gold, platinum, or silver, which have more positive potentials and react less readily in most environments. In galvanic corrosion, a potential difference develops between two metals in the same environment when in electrical contact. The metal with the more noble potential according to the SRP tables should behave as the cathode and the metal with the more active or negative potential should behave as the anode; under such conditions, anodic dissolution of the more active metal is greatly accelerated. This behavior is commonly exhibited by a number of familiar battery systems; for example, the Daniel cell is a controlled galvanic cell. When electrical contact is made between copper and zinc, a potential difference develops, equal to 1.1 volts, between the two metals and current flows from the zinc electrode to the copper electrode. The zinc electrode anodically dissolves, releasing electrons that are consumed by Cu^{++} ions, the net reaction being:



Most galvanic corrosion is unwanted and often unexpected. For example, a ship constructed of a nickel alloy and steel rivets becomes unseaworthy because the steel rivets are active and preferentially corrode at a high rate. The hot-water tank in your home can be troublesome if a steel tank is connected to copper tubing. In order to prevent galvanic corrosion, the potential difference between two metals must be made small or one of the metals must be electrically insulated.

Stress corrosion cracking (SCC) is another important form of corrosion that is particularly detrimental to load-bearing structures. Corrosion is often minimal but failure caused by crack propagation is likely to cause catastrophic results. SCC is a complex corrosion phenomenon involving mechanical, electrochemical, and metallurgical factors where synergistic action between a mechanical tensile stress and a corrosion environment leads to rapid failure. Since SCC is caused by the cojoint interaction of a stress and a corrosive, the removal of the stress or the corrosive results in the cessation of SCC. In addition, several other methods of reducing a structure's susceptibility to SCC are available and will be discussed in Chapter 8.

TABLE 1. STANDARD REDUCTION POTENTIAL SERIES

Reaction		Potential (volts) (SHE)
$\text{Au}^+ + \text{e}$	Au	1.680
$\text{Au}^{+3} + 3\text{e}$	Au	1.420
$\text{Pt}^{+2} + 2\text{e}$	Pt	1.200
$\text{Hg}^{+2} + 2\text{e}$	Hg	0.851
$\text{Pd}^{+2} + 2\text{e}$	Pd	0.830
$\text{Ag}^+ + \text{e}$	Ag	0.799
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}$	4OH^-	0.401
$\text{Cu}^{+2} + 2\text{e}$	Cu	0.158
$\text{Fe}^{+3} + 3\text{e}$	Fe	-0.036
$\text{Pb}^{+2} + 2\text{e}$	Pb	-0.126
$\text{Sn}^{+2} + 2\text{e}$	Sn	-0.136
$\text{Ni}^{+2} + 2\text{e}$	Ni	-0.230
$\text{Co}^{+2} + 2\text{e}$	Co	-0.280
$\text{Cd}^{+2} + 2\text{e}$	Cd	-0.403
$\text{Fe}^{+2} + 2\text{e}$	Fe	-0.409
$\text{Cr}^{+3} + 3\text{e}$	Cr	-0.740
$\text{Zn}^{+2} + 2\text{e}$	Zn	-0.763
$\text{Al}^{+3} + 3\text{e}$	Al	-1.706
$\text{Mg}^{+2} + 2\text{e}$	Mg	-2.380

Values Obtain from Handbook of Chemistry
and Physics, 56th Edition

CHAPTER 3

OBJECTIVES

The objective of this project is to design, construct and successfully install a new generation of lightweight weapons elevator platforms that will realize an increase in cost savings and provide many years of reliable use. Therefore, it is imperative that a thorough corrosion study take place concurrently during the design and fabrication stage to ensure that potential problems arising from corrosion are eliminated or significantly reduced. Further discussions will focus on the citing of specific examples of common problems that may be anticipated. In addition, a description and discussion of the experimental techniques that will prove to be most useful will be outlined.

CHAPTER 4

ENVIRONMENT

The U.S. Navy fights an on-going battle to control, prevent, and eliminate seawater corrosion. The corrosiveness of salt water is well documented and heightened interest in this area is supported by the voluminous amount of published literature. The continuous exposure of Naval ordnance, directly or indirectly, to seawater demands the scrutiny of all those involved in the design and maintenance of these structures. Therefore, a researcher should focus on those studies conducted in salt water environments, including immersion, atmospheric and cyclic wet and dry exposure of selected materials.

In addition, exposure of a weapons platform to fuels, oils, lubricants, and cleaning detergents must be considered; although identifiable problems may not develop initially, long-term effects of periodic exposure to these environments are unknown. The application of protective paints may also be adversely affected when exposed to organic solvents; however, it is presumed that currently used paints and application methods are well documented and problem areas realized. In addition, the weapons platform will be periodically exposed to fire fighting foams, e.g. AFFF, and, therefore, must receive proper attention.

CHAPTER 5

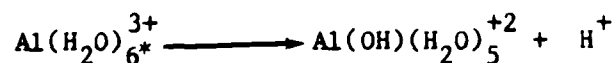
PITTING CORROSION

Metals exhibiting excellent corrosion behavior benefit from the presence of a corrosion resistant surface oxide, often occurring naturally. Aluminum, nickel, titanium, and chromium are familiar examples of metals that possess tightly adherent nonporous oxides that provide protection for the underlying metal in a large number of environments. The existence of a protective oxide makes these metals highly susceptible to localized attack at weak spots or damaged areas in the oxide layer. Unfortunately, many of the important metals and alloys utilized by the Navy are highly susceptible to pitting corrosion in marine environments.

A developing pit is especially pernicious because of the development of a highly localized region of low pH. The restricted access of oxygen into the pit, or "occluded cell," causes a segregation of the anodic and cathodic site. The pit becomes a specific site for anodic dissolution while the cathodic reduction reaction takes place in adjacent areas. The process of pitting can be described as autocatalytic in nature. The following is a simple description of how pitting corrosion proceeds as described by Fontana and Greene (1). The mechanism for pitting corrosion is schematically depicted in Figure 1. The metal is attacked by an aerated sodium chloride solution. Rapid dissolution occurs in a localized area, i.e., a pit, while oxygen reduction occurs on adjacent surfaces. An excess of positively charged ions soon develops because of the rapid dissolution of the metal within the pit. In order to maintain charge neutrality, chloride ions migrate into the growing pit and, as a consequence, a highly concentrated solution of metal cations develops within the pit; subsequently, hydrolysis of metal cations occurs, causing an increase in the concentration of hydrogen ions. For example, the dissolution of AlCl_3 in aqueous medium produces several hydrolysis reactions:



In general, the hydrolysis of aluminum cations can be represented by the following equation:



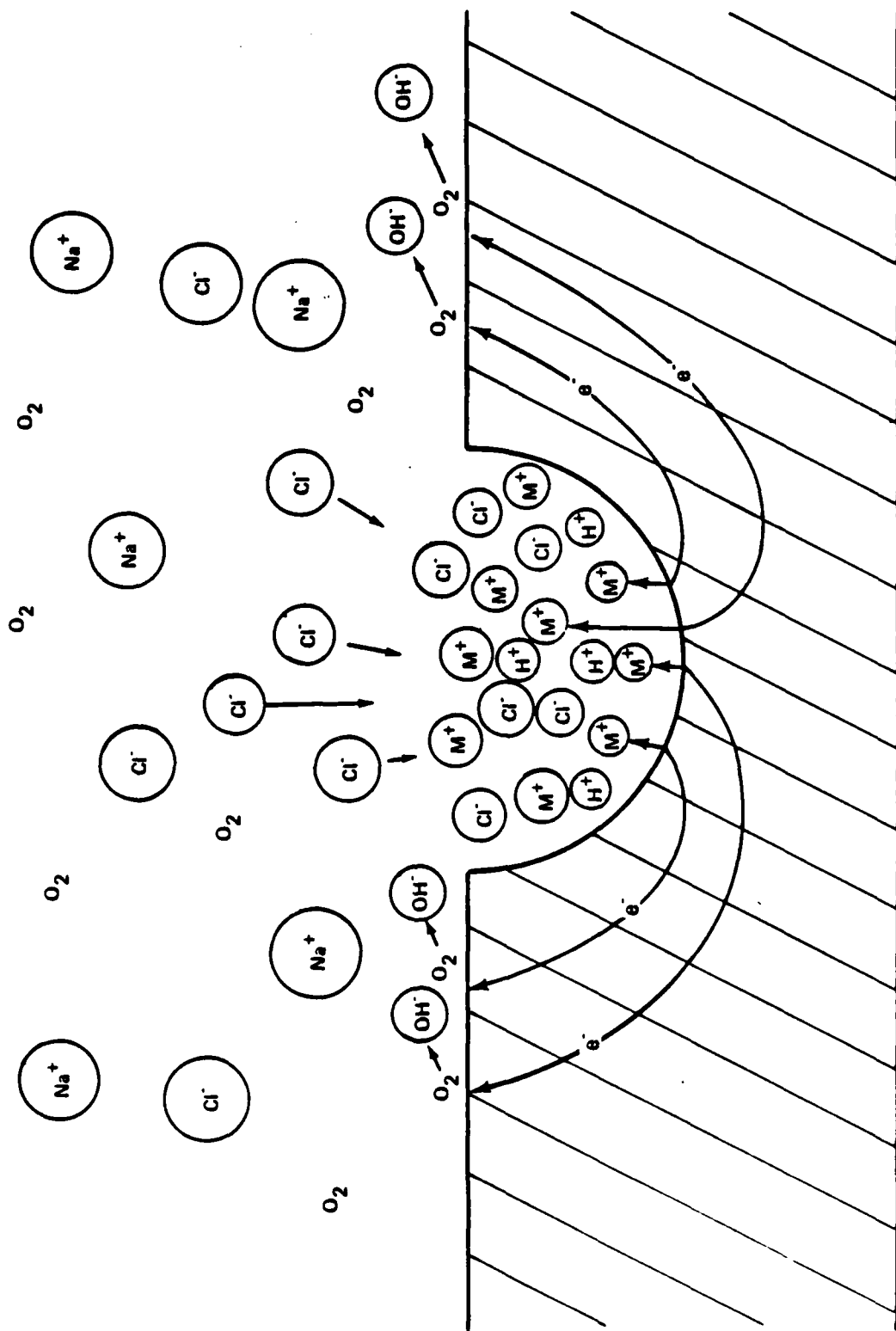


FIGURE 1. MODEL OF PITT PROPAGATION

In any case, the consequential liberation of H^+ ions promotes a lowering of the solution pH. Experimental evidence provided by Brown (2) on the localized corrosion of metals in chloride environments revealed that the pH of an "occluded cell" was approximately 3.5. Since low pH values and high chloride concentrations are particularly detrimental to most metals, the entire process accelerates with time. The highly concentrated solution within a pit significantly reduces the amount of dissolved oxygen; thus, no oxygen reduction occurs within the pit. In a sense, pitting corrosion cathodically protects the metal locally in those areas adjacent to the growing pit.

Although the discussion to this point provides for an explanation of the mechanism of pit growth, no mention is made of how this process is initiated. A number of theories exist, each providing important contributions to the understanding of pit initiation and propagation. Generally accepted views emphasize the importance of anion interaction with the metal and/or metal oxide, and inclusion of this anion interaction into a proposed mechanism is essential. G.C. Wood (3) feels that pit initiation occurs at weak spots, flaws in the metal and/or metal oxide. Flaws are defined as "residual," those arising from impurities found in the developing oxide that give rise to imperfect and nonhomogeneous films, or "mechanical," caused by inherent or accidental stresses incorporated into the oxide. Development of pits at these weak spots in the oxide lattice may occur because reactive anions can easily reach the anodic dissolution site.

T.P. Hoar et al. (4) describe the importance of an "ion-migration" theory. Highly mobile halide ions penetrate the oxide film (without concurrent exchange with the oxygen atoms of the oxide), thus increasing the concentration of halide contaminants in the oxide. This incorporation of halide ions into the oxide film greatly facilitates the transport of cations from the metal/metal oxide interface, which in turn enables the development of high corrosion current densities. Assuming the initial penetration of anions takes place through defects in the oxide layer lends credence to the observation that only localized areas are attacked. A prerequisite to halide penetration involves an initial adsorption of the ions onto the oxide surface.

However, another theory expounded by Hoar (5) favors a "mechanical" model to account for localized breakdown. Strong anion adsorption (dependent on the anion concentration in solution, potential difference at the solution/metal interface, and the nature of the anion) displaces hydroxide ions and water molecules at the interface, leading to a decrease in the interfacial free energy caused by the repulsive forces between charged particles. Peptization of the oxide layer by the strongly adsorbed anions creates cracks or fissures providing access for the solution to the base metal, providing a potential pit initiation site.

A four-step mechanism describing the pit initiation process for aluminum alloys has been provided by Nguyen and Foley (6). The proposed steps are: (1) anion, e.g., halides, adsorption at the oxide film/solution interface takes place; (2) a chemical reaction between the oxide and the anion leads to the formation of soluble complexes; (3) a thinning of the oxide film occurs; and (4) dissolution of aluminum in thinned areas takes place because Al ion migration is significantly accelerated. According to Richardson and Wood (7), preferential adsorption of anions may occur at defects or flaws in the oxide.

In summary, each of the proposed mechanisms of pit initiation described thus far emphasizes the important role that anion-oxide interactions assume during the course of pitting; thus, attack at weak spots in the oxide film or thinning of the oxide film by dissolution provide reasonable explanations for localized breakdown.

A literature survey suggests that even metals thought to be highly resistant to corrosion are susceptible to pitting corrosion under certain conditions. For example, L.C. Convington (8) describes the trouble experienced by the salt industry when pitting failure occurs in salt evaporators using titanium in heat exchanger tubes that carry hot saturated brine. F.J. Cornwell et al. (9) investigated the occurrence of pitting of copper tubes used for cold water service, an unusual problem because of the widely accepted use of copper in water distribution systems. In general, pitting is associated with the localized breakdown of highly passive films, such as those found on aluminum and stainless steels. Some materials are more resistant to pitting than others, and, as a guide, metals that exhibit a strong tendency to pit during corrosion tests should be avoided. Frequently the pitting resistance of a metal or alloy can be improved by the addition of certain alloying elements; for example, the addition of small amounts of molybdenum to stainless steels greatly increases resistance to pitting corrosion. Other metals that benefit from the addition of molybdenum to improve resistance include Hastelloy F, Nionel, Durimet 20, Hastelloy C, and Chlorimet 3.

Field observations of pitting corrosion indicate that pit growth occurs preferentially in the direction of gravity and, therefore, most pits develop and grow downward from a horizontal surface. Less common is the development of pits on vertical surfaces or the bottom side of a horizontal surface. The nature of pit propagation necessitates that the most stable growth direction take place under gravitational influence because the highly concentrated solution needed to sustain pit growth is more difficult to attain from vertical surfaces or the bottom of horizontal surfaces. Therefore, careful attention must be given to the exposed top-surface of the weapons platform and should be protected by the use of an appropriate paint system, especially when aluminum alloys are to be considered.

CHAPTER 6

CREVICE CORROSION

Metals and alloys susceptible to pitting corrosion are, in general, equally susceptible to crevice corrosion. According to Rosenfel'd (10), crevice corrosion is the most dangerous type of localized attack; it is an inherent characteristic of easily passivated alloys, such as stainless steels, titanium, and aluminum alloys. On the other hand, nonpassive metals, such as mild steel, under conditions when the environment is highly oxidizing, will also be susceptible to crevice corrosion.

Early evidence suggested that crevice corrosion only manifested itself in halide environments; however, more recent observations reveal that crevice corrosion may occur in other environments; for example, stainless steels are subject to crevice attack in sulfuric acid. I.A. Collins (11) noticed attack of stainless steel condenser tubes in a condensate containing 10% acetic and 10% formic acids. In addition, titanium was found to crevice corrode in sulfuric, oxalic, hydrochloric, and formic acids (12).

Crevice corrosion originates in areas shielded from the bulk environment, localized regions containing small volumes of solution where restricted diffusion of reactants occur. Attack takes place beneath bolt heads, rivets, washers, or lap joints, or between a metal and a nonmetal such as wood, concrete, plastic, rubber, or glass. The threat of crevice corrosion often discourages the designer from using a normally corrosion resistant material, i.e., titanium, in complex structures.

A detailed description of the mechanism responsible for crevice corrosion is given by Rosenfel'd (10). In general, crevice attack takes place in two main stages: (1) initiation by differential aeration and (2) propagation by acidification of the local environment. Fontana and Greene (1) provide a simple conceptual model to explain the process of crevice corrosion: Two metal plates riveted together are placed in aerated neutral seawater (see Figures 2-3). Metal, M, dissolves, and reduction of oxygen occurs in the crevice as well as over the exterior of the two metals. After a short time, the oxygen within the crevice is consumed because of restricted diffusion, and oxygen reduction is thus limited to areas outside of the crevice, Figure 3. However, overall oxygen reduction continues essentially undisturbed because of the small original contribution made by oxygen reduction within the crevice, and, as a consequence, metal corrosion continues as before. An excess of metal ions collect within the crevice where electroneutrality is maintained by the migration of chloride ions to the crevice from the bulk solution. As a result of the high concentration of metal ions, hydrolysis of metal cations produces a crevice solution of low pH. The synergistic effects of low solution pH and high chloride concentration

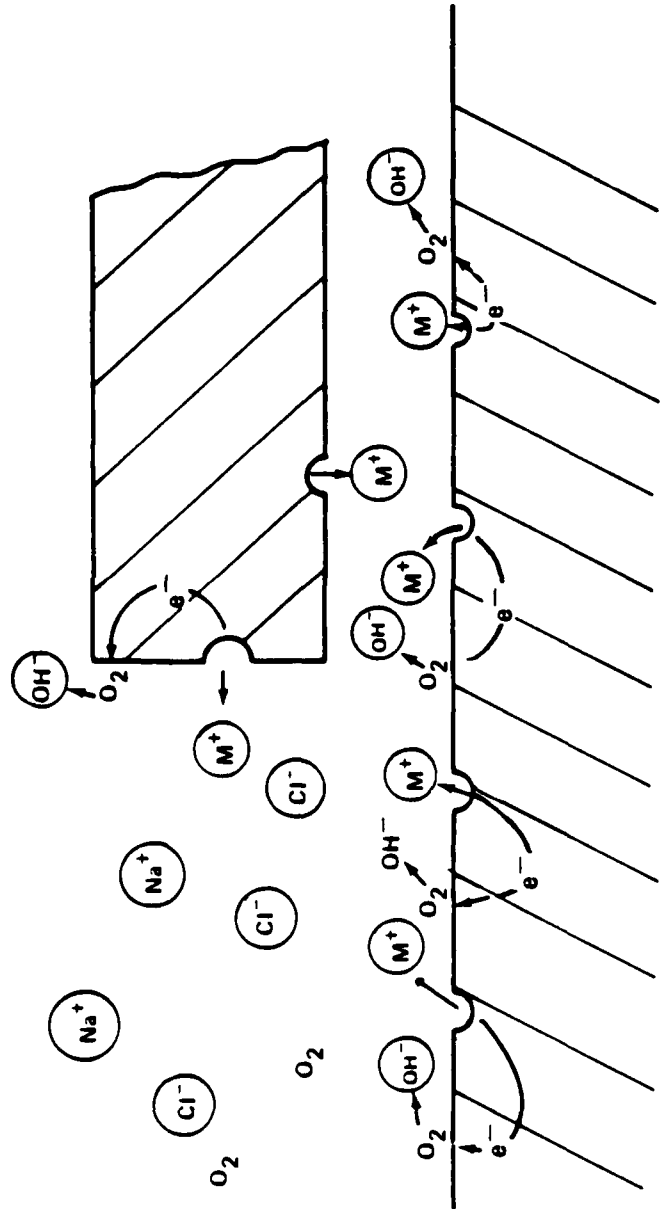
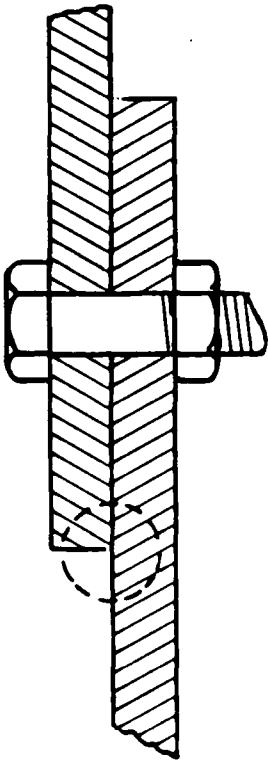


FIGURE 2. MODEL OF CREVICE INITIATION

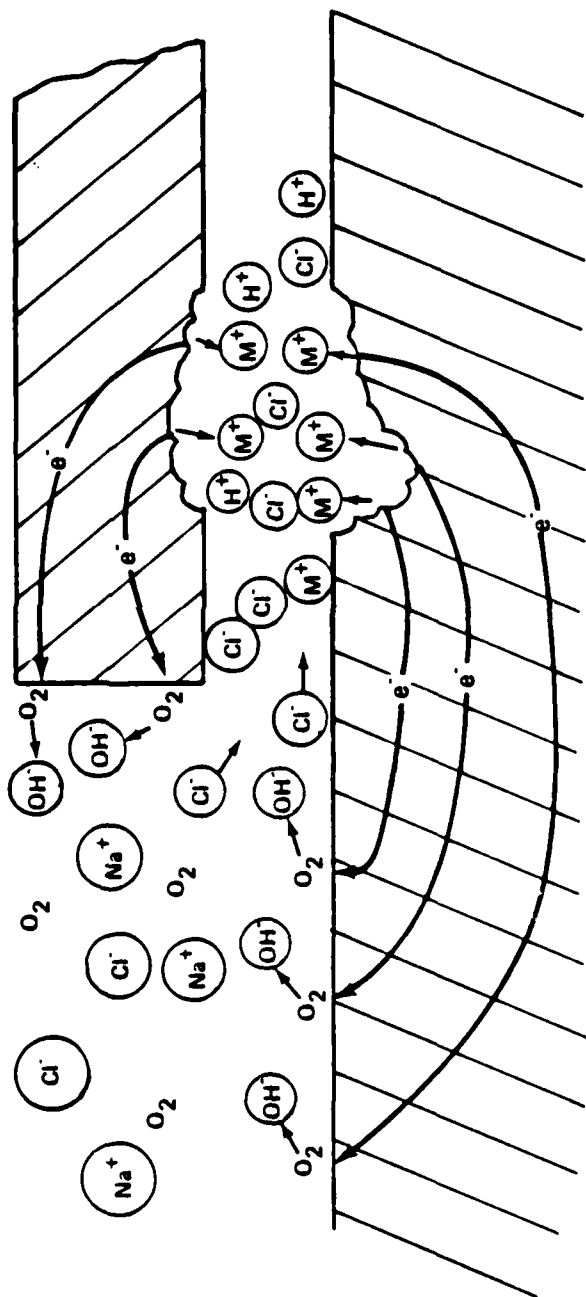


FIGURE 3. MODEL OF CREVICE PROPAGATION

produces an aggressive environment that rapidly accelerates the corrosion process.

The compositional change of the crevice solution, as corrosion progresses, alters the electrochemical reaction kinetics occurring within the crevice as well as on the outside surface of the metal; as a result, a potential difference develops and the crevice becomes more active, i.e., more negative relative to the exterior. A complex situation arises because of the large potential difference such that the crevice and exterior metal can be treated separately; that is, the exterior is more noble and assumes the role of the cathode and the crevice, more active, becomes the anode. The driving force behind the propagation of crevice corrosion is provided by this potential difference. Therefore, factors that normally accelerate the kinetic of cathodic reactions, such as high flow rate (stirring), high concentration of depolarizers (oxygen), or increased surface area, tend to increase the rate of anodic dissolution within the crevice. An investigation made by McCafferty (13) on the crevice corrosion of iron in neutral chloride solutions provides an excellent example of how the crevice and "external" cathode can be treated separately for experimental studies.

The commonality that exists among the number of different forms of localized corrosion arises from the similarity of their local solution chemistries; reports reveal that crevices, pits, and stress corrosion cracks acidify locally, a result of the restricted flow of reactants. Each of these types of attack is particularly dangerous and should be avoided. It is generally accepted that crevice corrosion occurs more readily and more frequently than pitting corrosion and Wilde (14) makes an important distinction between a material's pitting and crevice susceptibility. For example, the addition of molybdenum to stainless steel to prevent pitting is well established; however, Wilde (14) discovered experimentally that when the situation arises where a pit-resistant alloy, e.g. 30Cr-3Mo-Fe, is configured such that a crevice is present, local attack in this area is highly probable. Although pitting and crevice corrosion seem to propagate by the same mechanism of accelerated anodic dissolution in regions of restricted diffusion, their initiation processes are quite different, and this helps to explain why crevice corrosion often occurs preferentially to pitting. A growing crevice will cathodically protect the remainder of the surface, thus effectively inhibiting pit initiation. In light of these observations, it is obvious that the occurrence of crevice corrosion is more likely than pitting corrosion when potential crevice sites exist.

Methods and techniques that are commonly employed to prevent crevice corrosion include rational design selection, electrochemical protection, sealing of clearances, and use of solution inhibitors. Fontana and Greene (1) provide a useful guide, which should be acknowledged before a weapons platform design selection is made. Some of its highlights are listed below:

(1) Use welded butt joints instead of riveted or bolted joints. Sound welds and complete penetration are necessary to avoid porosity and crevices on the inside (if welded only from one side).

(2) Close crevices in existing lap joints by continuous welding, caulking, or soldering.

- (3) Design structures or vessels for complete drainage; avoid sharp corners and stagnant areas where solution may accumulate.
- (4) Inspect frequently and remove all deposits.
- (5) Use solid nonabsorbent gaskets, such as teflon, wherever possible.

CHAPTER 7

GALVANIC CORROSION

Dissimilar metal corrosion is a persistent problem faced by design engineers because of the need to utilize a variety of different metals to construct complex structures as dictated by the large number of mechanical, metallurgical, and economical requirements. Care must be exercised when making material selections; however, proper testing of candidate materials should recognize problem areas in advance.

When two dissimilar metals are placed in the same environment, a potential difference develops and when electrical contact is made between the two metals a current flows; the direction of current flow is dependent on the metal's electrochemical activity in that environment and, in general, can be predicted using the measured corrosion potentials of the uncoupled metals. A metal exhibiting a more negative, or active, corrosion potential should act as the anode and the direction of current flow will be from anode to cathode, the metal with the more positive, or noble, corrosion potential. Corrosion of the more active metal will be significantly increased and attack at the more noble metal will be decreased, as compared to their uncoupled behavior.

Initially, the standard reduction potential tables can be used to predict which metal would act as the anode or the cathode in an electrically or physically connected couple. This approach turns out to be dangerous and often incorrect. These potentials are measured against the standard hydrogen electrode in aqueous solutions of unit activity of the metal of interest, and this is not representative of typically encountered environments; in addition, the behavior of alloys cannot be predicted. A number of investigators have obtained the data needed to assemble and construct tables that predict the galvanic corrosion tendencies of commonly used metals and alloys. One such galvanic series was constructed by the International Nickel Company at Harbor Island, N.C., and is based on potential measurements and corrosion tests in seawater. This series is reproduced in Table 2. Relative positions of the metals are used rather than their potentials; brackets designate those metals that are similar in base composition and behavior. When metals within a given bracket are coupled, there is little chance of galvanic corrosion occurring. This table and others like it only apply to the specific environment in which the test data was collected, and the position of a metal or alloy or groups of metals or alloys may change as the environment changes. Ideally, it would be advantageous to construct galvanic tables for all possible combinations of environment and metal or alloy; however, this would prove to be quite tedious and impractical; therefore, individual tests should be made on the metal or alloy of choice in the environment of interest as needed.

TABLE 2. GALVANIC SERIES*

↑ Noble or cathodic	Platinum Gold Graphite Titanium Silver [Chlorimet 3 (62 Ni, 18 Cr, 18 Mo) Hastelloy C (62 Ni, 17 Cr, 15 Mo) 18-8 Mo stainless steel (passive) 18-8 stainless steel (passive) Chromium stainless steel 11-30% Cr (passive) Inconel (passive) (80 Ni, 13 Cr, 7 Fe) Nickel (passive) Silver solder [Monel (70 Ni, 30 Cu) Cupronickels (60-90 Cu, 40-10 Ni) Bronzes (Cu-Sn) Copper Brasses (Cu-Zn) Chlorimet 2 (66 Ni, 32 Mo, 1 Fe) Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn) Inconel (active) Nickel (active) Tin Lead Lead-tin solders [18-8 Mo stainless steel (active) 18-8 stainless steel (active) Ni-resist (high Ni cast iron) Chromium stainless steel, 13% Cr (active) [Cast iron Steel or iron 2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn) Cadmium Commercially pure aluminum (1100) Zinc Magnesium and magnesium alloys
Active or anodic ↓	

* From Ref 1.

In order to effectively estimate the rate of galvanic corrosion, the current produced by galvanic action must be monitored. A large sustained galvanic current suggests that severe corrosion will take place. Under normal circumstances this would be the case. Equally feasible is the occurrence of an initially high current that rapidly decreases with time because of the accumulation of adherent corrosion products on the anode. In this case, a low rate of galvanic corrosion is likely. This observation strongly indicates that galvanic couples must be monitored over an extended period of time. Mansfeld and Kenkel (1) and Baboian (16) review the experimental techniques that can be used to follow galvanic corrosion currents with time.

The magnitude of the galvanic current density generated for different couples is not, in most cases, directly related to the corrosion current density, i.e., corrosion rate. Mansfeld and others (17-20) present theoretical discussions pertaining to the relationship between measured galvanic currents and corrosion rates. Three representative cases, as outlined by Mansfeld (18-20), typical of galvanic behavior will be highlighted below. In the first case, the galvanic couple potential, E_{couple} , is far removed from the corrosion potentials, E_{corr} , of uncoupled metals. It is assumed that only an oxidation reaction (metal dissolution) occurs at the anode and only a reduction reaction occurs at the cathode. The measured galvanic current, I_g , will equal the dissolution current, I_d^a , for the anode of the couple provided the individual anodic and cathodic reactions exhibit Tafel behavior (where the reactions are under charge transfer control):

$$I_g = I_d^a \quad [1]$$

Corrosion of metals exposed to neutral aerated solutions is strongly influenced by diffusional control, i.e., the limiting current density for oxygen diffusion. For the second case, it is assumed that the only reaction occurring at the cathode is the reduction of oxygen; in addition, it is assumed that both anodic and cathodic reactions occur at the anode. However, the individual rates for oxygen reduction at the anode and cathode are considered to be unequal; this assumption must be true because the observed effects of diffusional control on generated galvanic currents would not be possible if by chance the rate of oxygen reduction were equal for all metals; thus the normally observed dependence of galvanic currents on the nature of the metal cathode would not be observed. As a result, the anodic dissolution current, I_d^a , for the anode must be equal to the sum of reduction currents at the anode, I_c^a , and cathode, I_c^c :

$$I_d^a = I_c^a + I_c^c \quad [2]$$

From equation [2] it follows:

$$i_d^a A^a = i_c^a A^a + i_c^c A^c \quad [3a]$$

$$i_d^a = i_c^a + i_c^c \quad [3b]$$

where A_a and A_c are the surface areas for the anode and the cathode. From equation [3b], the dissolution current density for the anode, i_d^a , is equal to the sum of the cathodic current densities at the anode and cathode for equivalent surface areas. For a diffusion controlled process, the measured galvanic current density will be equal to the limiting diffusion current density for oxygen reduction at the cathode:

$$i_g = i_{L,O_2}^c = i_c^c \quad [4]$$

where i_{L,O_2}^c is the limiting diffusion current density for oxygen reduction at the cathode. For the uncoupled anode, it is assumed that the cathodic current density is determined by the limiting diffusion current density and, as a consequence, can be taken to be equivalent to the corrosion current density:

$$i_c^a = i_{L,O_2}^a = i_{corr}^a \quad [5]$$

where i_{L,O_2}^a is the limiting diffusion current density for oxygen reduction at the anode and i_{corr} is the uncoupled corrosion rate for the anode. Since it is assumed that equations [3b] and [4] are valid, the galvanic current density is, therefore, equal to the difference between the oxidation current densities, i_a^a , and the reduction current densities, i_c^a , of the anode at E_{couple} :

$$i_{L,O_2}^a = i_g = i_a^a - i_c^a \quad [6]$$

Rearranging equation [6] and substituting with equation [5]:

$$i_a^a = i_d^a = i_g + i_c^a \quad [7a]$$

$$i_d^a = i_g + i_{L,O_2}^a \quad [7b]$$

$$i_d^a = i_g + i_{corr}^a \quad [7c]$$

Equations [7b] and [7c] arise from the assumption that reactions occurring at the anode can be described by equation [5]. Therefore, the dissolution current density for the anode in a galvanic couple is equal to the sum of the measured galvanic current density and the corrosion current density for the uncoupled anode (see Equation [7c]).

For case III, E_{couple} is located so near to E_{corr} of the uncoupled anode that both anodic and cathodic reactions occur at an appreciable rate at the anode. Thus Tafel behavior is not exhibited for the dissolution reaction at the anode. It is then observed that the dissolution current will fall between:

$$I_g \leq I_a^a \leq I_g + I_{\text{corr}}^a$$

where I_{corr}^a is the corrosion current of the uncoupled anode. In general, these three examples can be used to relate measured galvanic currents to actual corrosion currents; hence, calculations of corrosion rates using Faraday's equation are possible.

An important factor that influences the extent to which galvanic corrosion occurs involves the polarizability of the metal cathode of the couple. A highly efficient cathode will produce high cathodic currents serving to drive the anodic reaction, i.e., an increase in the anodic dissolution rate. For example, titanium is a highly noble metal even when exposed to seawater and when coupled to a less corrosion-resistant metal or alloy, one would intuitively expect that rapid attack would occur, but this is not the case. The corrosion rate is low because titanium is highly polarized in seawater; that is, titanium is a poor catalyst for the oxygen reduction reaction. Therefore, factors that affect the kinetics of the cathodic reaction significantly influence the rate of anodic dissolution.

The magnitude of galvanic corrosion is in many cases greater in localized areas; that is, galvanic corrosion usually occurs in the immediate vicinity of the metal/metal couple interface, a region where the galvanic currents are the strongest. As a general rule of thumb, the severity of galvanic corrosion decreases as the distance from the couple interface increases.

The cathode-to-anode area ratio of a galvanic couple is perhaps the most important factor that influences the rate of galvanic corrosion. For example, if two steel panels are joined by copper rivets and exposed to seawater, the steel panels will corrode; however, the bond between the two panels will remain intact. Copper is more noble than steel, and therefore acts as the cathode. The generated anodic currents at the steel anode are distributed over a large area, and as a result, small anodic current densities are produced. These small anodic current densities translate into small corrosion rates. On the other hand, connecting two copper panels together with steel rivets causes rapid deterioration of the steel rivets because of the large cathode-to-anode area ratio. The anode must now sustain large current densities, so significant corrosion of the steel rivets occurs and the bond between the copper plates fails.

Fontana and Greene (1) provide an excellent example of an industrial galvanic problem:

"... a plant installed several hundred large tanks in a major expansion program. Most of the older tanks were made of ordinary steel and completely coated on the inside with a baked phenolic paint. The solutions handled were only mildly corrosive to steel,

but contamination of the product was a major consideration. The coating on the floor was damaged also because of mechanical abuse, and some maintenance was required. To overcome this situation the bottoms of the new tanks were made of mild steel clad with 18-8 stainless steel. The tops and sides were of steel, with the sides welded to the stainless clad bottom as illustrated by Figure 4. The steel was coated with the same phenolic paint, with the coating covering only a small portion of the stainless steel below the weld.

A few months after start-up of the new plant, the tanks started failing because of perforation of the side walls. Most of the holes were located within a 2-in. band above the weld... Some of the all-steel tanks had given essentially trouble-free life for periods as long as 10 to 20 years as far as sidewall corrosion was concerned.

The explanation for the above failure is as follows. In general, all paint coatings are permeable and may contain some defects. For example, this baked phenolic coating would fail in double-distilled water service. Failure of the new tanks resulted from the unfavorable area effect. A small anode developed on the mild steel side plates. This area was in good electrical contact with the large stainless steel bottom surface. The area ratio of cathode to anode was almost infinitely large, causing very high corrosion rates in the order of 1000 mpy."

This example demonstrates that when a structure containing dissimilar metals is to be coated, the more noble metal(s) should be coated in preference to the more active metal; better yet, the entire structure should be coated with particular care given to the active metal portion to avoid small unexposed metal areas that may act as anodic sites, giving rise to perforation corrosion.

Reboul (21) and Mansfeld et al. (17) provide excellent reviews on the galvanic corrosion behavior of aluminum coupled to a large number of metals and alloys exposed to seawater and tap water. Mansfeld et al. (17) constructed a table rank-ordering 95 aluminum alloys coupled to a variety of metals and alloys. This table is reproduced as Table 3 of this report. A general ranking of metals coupled to aluminum alloys can be given in order of decreasing galvanic current: $\text{Ag} > \text{Cu} > 4130 \text{ steel} \gg \text{stainless steel} \approx \text{Ni} > \text{Inconel 718} \gg \text{Ti-6Al-4V} \approx \text{Haynes 188} > \text{Sn} > \text{Cd}$. An important observation made by Mansfeld et al. (17) revealed that aluminum alloys 1100 and 6061, which have low corrosion rates when not coupled to a noble metal, exhibited a significant increase in their corrosion rates when coupled to noble metals than did AA-2024 and AA-2219, which have much higher corrosion rates when uncoupled. Reboul (21) also found that stronger galvanic currents were produced for AA-5086 and AA-1050 than with copper containing AA-7075 and AA-2024. Mansfeld et al. (17) summarize the behavior of aluminum alloys as follows: AA-1100 is only compatible with Cd, AA-6061 alloy with AA-7075, AA-2024, and AA-2219, and AA-7075 is only compatible with other aluminum alloys and Zn. In general, it is almost impossible to couple aluminum and its alloys to any other metal and expose it to seawater without adequate protection, i.e., painting or insulating the dissimilar metals from one another.

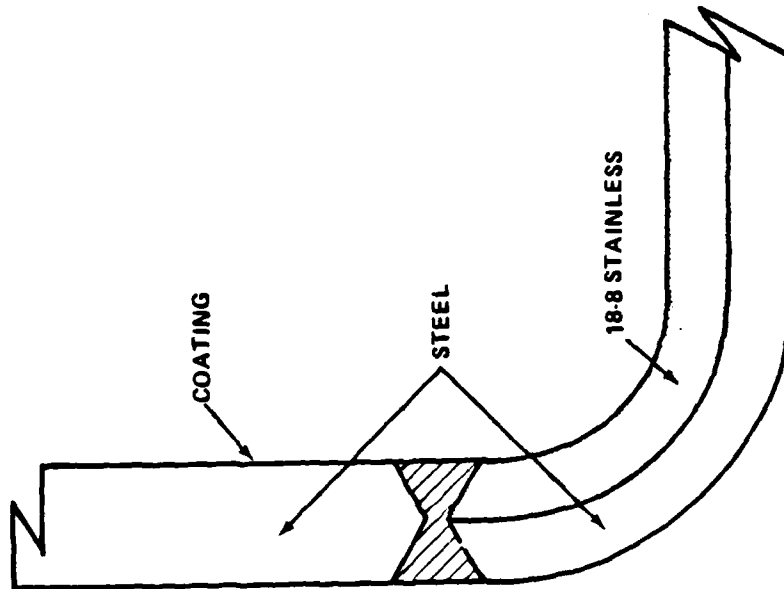


FIGURE 4. DETAIL OF WELDED STEEL AND STAINLESS CLAD TANK CONSTRUCTION
FROM REF 1.

In seawater, most aluminum alloys are anodic to most other metals. Therefore, aluminum alloys will be severely attacked, whereas the more noble metal of the couple will be protected. A particularly dangerous situation may develop when copper or brass is immersed in the same solution as aluminum. Dissolved copper ions in solution may plate out onto the aluminum surface, causing the formation of local galvanic cells. Contact between aluminum and nickel alloys is especially dangerous and should be avoided. Several methods can be employed to protect aluminum; for example, the contact points between aluminum and the dissimilar metal can be insulated, or barrier coatings can be used to improve the resistance of aluminum to galvanic attack, such as the application of a zinc phosphate coating or aluminizing steel components by flame spraying. Chromium plating has been used; however, it is effective only when the coating is thick and nonporous.

Galvanic corrosion of a weapons platform will occur in contact areas between dissimilar metals, particularly steel and aluminum; however, insulation of potential contact points or thorough paint protection of the galvanic parts will prove to be highly beneficial. In summary, the magnitude of galvanic corrosion is dependent on the potential difference between dissimilar metals, the kinetics of the individual anodic and cathodic reactions, the nature of the environment, i.e., highly conductive solutions will produce large currents, and the cathode-to-anode area ratio. The measurement of corrosion potentials can only be used to predict the direction of galvanic current flow; in no way can it be used to predict the rate of galvanic corrosion. Continuous monitoring of galvanic currents provides the only reliable and accurate method of assessing the galvanic effect.

TABLE 3. GALVANIC SERIES FOR AL ALLOYS IN 3.5% NaCl*

OVERALL RANKING	COUPLE	\bar{i}_g (A/cm ²)	r_A (mdd)
1	7075-Ag	63.8	68.8
2	6061-Ag	54.5	65.6
3	1100-Ag	53.8	55.3
4	2024-Ag	50.6	64.3
5	2219-Ag	47.4	69.4
6	7075-Cu	45.0	58.8
7	6061-Cu	43.6	47.7
8	2024-Cu	41.0	63.1
9	1100-Cu	39.8	40.4
10	2219-Cu	36.3	49.6
11	1100-4130	27.9	30.2
12	7075-4130	25.0	26.0
13	2024-4130	24.5	38.1
14	6061-4130	24.3	27.0
15	7075-Ni	22.0	22.6
16	6061-Ni	21.9	29.7
17	2219-4130	20.3	34.6
18	2024-Ni	18.0	29.0
19	1100-PH13-8Mo	17.5	18.9
20	7075-A286	17.0	18.1
21	7075-SS304L	17.0	16.1
22	7075-SS347	16.8	16.2
23	1100-SS301	16.6	20.8
24	7075-PH13-8Mo	16.5	6.2
25	6061-PH13-8Mo	16.0	19.8
26	7075-SS301	15.3	17.1
27	6061-A286	14.7	18.7
28	6061-SS347	14.1	21.2
29	2219-SS347	13.9	25.0
30	1100-Ni	13.9	15.9
31	1100-A286	13.8	14.5
32	2219-A286	13.4	22.0

\bar{i}_g · AVERAGE GALVANIC CURRENT DENSITY

r_A · AVERAGE RATE OF CORROSION

* From Ref. 17.

TABLE 3 (Cont.)

OVERALL RANKING	COUPLE	\bar{i}_g (A/cm ²)	r_A (mdd)
33	2024-SS301	13.2	30.4
34	2024-PH13-8Mo	12.9	21.0
35	2024-SS304L	12.8	26.5
36	6061-SS301	12.4	17.3
37	1100-SS304L	12.3	17.9
38	2219-SS304L	12.2	21.4
39	7075-INCO 718	12.2	11.6
40	1100-SS347	12.0	14.7
41	2219-Ni	11.3	30.4
42	6061-SS304L	11.3	16.1
43	2219-SS301	11.0	18.6
44	2024-SS347	10.5	24.2
45	2219-INCO 718	10.4	24.0
46	1100-INCO 718	10.4	11.4
47	2024-A286	10.3	25.4
48	2024-INCO718	9.3	20.4
49	7075-HAYNES 188	8.9	6.9
50	2219-PH13-8Mo	8.4	17.2
51	7075-Ti-6-4	8.3	8.5
52	1100-Ti-6-4	8.3	8.1
53	6061-INCO 718	8.1	7.0
54	1100-HAYNES 188	6.1	7.1
55	7075-Cd	5.9	5.9
56	2024-HAYNES 188	5.8	14.6
57	7075-Sn	5.8	7.3
58	2024-Ti-6-4	5.3	17.2
59	6061-Ti-6-4	5.2	8.3
60	6061-HAYNES 188	5.0	7.7
61	2219-Sn	4.7	7.7
62	2219-Ti-6-4	4.4	18.4
63	2219-HAYNES 188	4.0	5.4
64	7075-2219	3.8	4.2
65	1100-Sn	3.4	4.0
66	6061-2219	3.1	0.5
67	2024-2219	2.8	16.7
68	2024-Sn	2.75	13.1
69	7075-2024	2.6	1.3
70	2024-6061	1.95	18.5
71	6061-2024	1.95	+0
72	6061-Sn	1.59	-5.9

\bar{i}_g • AVERAGE GALVANIC CURRENT DENSITY

r_A • AVERAGE RATE OF CORROSION

* From Ref. 17.

TABLE 3 (Cont.)

OVERALL RANKING	COUPLE	\bar{i}_g (A/cm^2)	r_A (mdd)
73	1100-2219	1.20	3.1
74	1100-2024	1.15	1.8
75	6061-1100	0.66	3.7
76	7075-6061	0.66	1.8
77	6061-Cd	0.28	4.0
78	1100-7075	0.26	4.1
79	7075-110	-0.26	2.3
80	1100-6061	-0.66	2.3
81	6061-7076	-0.66	1.4
82	1100-Cd	-0.90	1.3
83	2024-1100	-1.15	10.6
84	2219-1100	-1.5	8.6
85	6061-Zn	-1.51	6.6
86	1100-Zn	-1.52	8.6
87	2024-Cd	-1.54	5.9
88	2219-Cd	-2.1	5.5
89	2219-2024	-2.3	8.7
90	2024-7075	-2.6	9.0
91	2219-6061	-3.1	8.9
92	7075-Zn	-3.4	4.0
93	2219-7075	3.8	11.4
94	2024-Zn	-6.8	19.3
95	2219-Zn	11.1	34.2

\bar{i}_g · AVERAGE GALVANIC CURRENT DENSITY

r_A · AVERAGE RATE OF CORROSION

* From Ref. 17.

CHAPTER 8

STRESS CORROSION CRACKING

The phenomenon of stress corrosion cracking (SCC) is typically exhibited by alloys and not by pure metals. When alloys are subjected to a tensile stress in a specific corrosive environment, SCCs may develop that propagate in either an intergranular or transgranular fashion and almost always grow in a direction perpendicular to the tensile stress. The tensile stress may be a design operating stress or residual stresses originating from cold-working, heat treatments, or welding. The aggressive environment does need to be highly concentrated nor severely corrosive. SCC can occur when structures are fully immersed in an aggressive environment or exposed to atmospheric corrodants such as salt air, high relative humidity, or ammonia vapors. To date there appears to be no specific class of environments that is responsible for SCC. Each alloy system is often susceptible to SCC in a wide range of environments, including aqueous electrolytes, organics with trace amounts of water, fused salts, nonaqueous inorganic liquids, and liquid metals. Tables 4 and 5 list a number of alloy systems and the environments in which they exhibit SCC.

SCC occurs primarily in alloys with highly protective oxides such as aluminum, titanium, stainless steel, and copper alloys. During SCC, the alloy surface remains essentially unattacked while insidious crack propagation through the structure occurs; therefore, corrosion is usually minimal but an important step in the propagation of SCCs. An introduction to stress corrosion cracking phenomena is provided by several authors (1, 22-24).

There is no generally accepted theory to account for all SCC. Theories that have been proposed to explain the nature of SCC number almost as many as the alloys that exhibit SCC for specific environments. A summary of some of the most important theories is listed below (24).

- (1) Mechano-Electrochemical. A tensile stress opens a crack and exposes bare metal. The corrodant then reacts with the metal at the crack-tip, leading to a dissolution of the metal.
- (2) Film Rupture. A brittle corrosion product film forms on the alloy and breaks under stress at the crack-tip, and the bare metal reacts with the corrodant to form a new film and the cycle repeats.
- (3) Embrittlement. Hydrogen atoms are absorbed at the crack-tip, causing embrittlement in a small volume of metal that cracks under the influence of the tensile stress.

TABLE 4. ENVIRONMENTS THAT MAY CAUSE STRESS CORROSION OF METALS AND ALLOYS

Material	Environment
Aluminum alloys	NaCl-H ₂ O ₂ solutions NaCl solutions Seawater Air, water vapor
Copper alloys	Ammonia vapors and solutions Amines Water, water vapor
Gold alloys	FeCl ₃ solutions Acetic acid-salt solutions
Inconel	Caustic soda solutions
Lead	Lead acetate solutions
Magnesium alloys	NaCl-K ₂ CrO ₄ solutions Rural and coastal atmospheres Distilled water
Monel	Fused caustic soda Hydrofluoric acid Hydrofluosilicic acid
Nickel	Fused caustic soda
Ordinary steels	NaOH solutions NaOH-Na ₂ SiO ₂ solutions Calcium, ammonium, and sodium nitrate solutions Mixed acids (H ₂ SO ₄ -HNO ₃) HCN solutions Acidic H ₂ S solutions Seawater Molten Na-Pb alloys

From Ref. 1.

TABLE 4 (Cont.)

Material	Environment
Stainless steels	Acid chloride solutions such as MgCl_2 and BaCl_2 Seawater H_2S $\text{NaOH-H}_2\text{S}$ solutions Condensing steam from chloride waters
Titanium alloys	Red fuming nitric acid Seawater N_2O_4 Methanol- HCl

From Ref. 1.

TABLE 5. SOME COMMON EXAMPLES OF STRESS CORROSION SYSTEMS

Alloy	Medium	Comments	Mode of failure (intergranular/ transgranular)
High strength steels	Water		I
High strength aluminum alloys	Chloride solutions, organic solvents	Appears to be due moisture	I
Copper alloys - Cu-Zn, Cu-Al, Cu-Si α -phase	Ammoniacal solutions Some solutions amine		I/T
Magnesium alloys	Chloride solutions	May be due to moisture	I/T
Cu ₃ Au alloys	FeCl ₃ solutions		I/T
Mild Steels	Hydroxide and nitrate solutions	Phosphates and carbonates also cause cracking in some potential ranges	I/T
Austenitic stainless steels	Hot chloride solutions Hydroxide solutions		T/I
Zirconium alloys	FeCl ₃ solutions Iodine at 350°C		I/T
Titanium alloys	Chloride solutions Organic solutions Fused chloride melts N ₂ O ₄ Hot solid chlorides		I/T

From Ref. 22.

- (4) Periodic Electrochemical-Mechanical. Electrochemical dissolution of a metal, e.g. pitting. Stress concentrations build up at the base of a pit, thus leading to rapid cracking followed by additional dissolution and mechanical cracking.
- (5) Adsorption. Adsorption of certain species at specific sites reduces the surface free energy of the metal, thus increasing the tendency of the metal to form a crack under a tensile stress.

More comprehensive treatments on the theories and mechanisms of SCC are presented by Spiedel (25) and Scully (26). In addition, an excellent review of SCC exhibited by high strength steels and titanium and aluminum alloys is provided in a publication edited by Brown (27).

Aluminum alloys. The high strength 2000 and 7000 series aluminum alloys are more vulnerable to SCC than any other of the aluminum alloys. In general, aluminum alloys with highly textured morphologies exhibit varying tendencies toward SCC, depending on the direction of the tensile stress in relation to the texture direction. It has been stated by Foley and Brown (24) that aluminum alloys stressed parallel to the short transverse grain direction are more susceptible to SCC and most resistant to SCC when stressed parallel to the longest grain dimension; in addition, intermediate susceptibility to SCC occurs when the alloy is stressed parallel to the long transverse grain direction. In view of these facts, the design of a new weapons platform utilizing rolled aluminum alloy products should avoid excessive stresses in the short transverse direction. Table 6 lists the susceptibility of various aluminum alloys when stressed in the short transverse direction.

According to Scully (22), aluminum alloys exhibit intergranular SCC when exposed to Cl^- , Br^- , and I^- ions but not F^- ions; and maximum susceptibility for aluminum alloys occurs near to peak hardness; the nature of intergranular precipitates and the zones adjacent to them are also important. It is well established that aluminum alloys are susceptible to SCC when exposed to seawater or high relative humidity, two environments that should concern the designer of all Naval structures.

High Strength Steels. All steels that are strengthened by heat treatments or precipitation hardening are susceptible to SCC in aqueous environments or high relative humidity. According to Foley and Brown (24), above about 1200 MPa yield strength, the occurrence of SCC becomes highly probable but becomes increasingly acute above 1400 MPa. Therefore, any structure constructed with high strength steels should be exposed to low tensile or bending stresses and/or elimination of contact with aqueous environments. Compressive stresses are not considered to be damaging.

Mild Steels. Mild steels are susceptible to SCC in hot concentrated aqueous alkalis and hot concentrated nitric acids. These conditions are particularly hazardous to boilers and steam equipment in regions of high stress such as near rivets or seams. According to Uhlig and Revie (23), when mild steel is stressed in tension beyond its elastic limit, it suffers SCC along intergranular paths. The tensile stress may arise from operational stresses or residual stresses. Mild steels are also vulnerable to SCC when exposed to anhydrous liquid ammonia and aqueous mixtures of carbon dioxide and carbon monoxide.

TABLE 6. CATEGORIES OF AQUEOUS SUSCEPTIBILITY OF
COMMERCIAL WROUGHT ALUMINUM ALLOYS IN
PLATE FORM - SHORT TRANSVERSE ORIENTATION

Susceptibility category	Alloy	Temper
very low	1100	all
	3003, 3004, 3005	all
	5000, 5050, 5052, 5154	all
	5454, 6063	
	5086	O, H32, H34
	6061, 6262	O, T6
	Alclad: 2014, 2219, 6061, 7075	all
low	2219	T6, T8
	5086	H36
	5083, 5456	controlled
	6061	T4
	6161, 5351	all
	6066, 6070, 6071	T6
	2021	T8
	7049, 7050, 7075	T73
moderate	2024, 2124	T8
	7050, 7175	T736
	7049, 7075, 7178	T6
appreciable	2024, 2219	T3, T4
	2014, 7075, 7079, 7178	T6
	5083, 5086, 5456	sensitized
	7005, 7039	T5, T6

From Ref. 28.

Stainless Steels. Austenitic stainless steels are particularly vulnerable to SCC when exposed to hot aqueous chloride or hydroxide environments and generally exhibit transgranular cracking. For example, 18-8 stainless steel will crack within hours upon exposure to boiling FeCl_3 or MgCl_2 (23). It has been observed that high oxygen content is necessary for the SCC of austenitic stainless steels (23 and 24); for example, SCC can occur at low chloride ion concentrations when high oxygen content is available but SCC is often eliminated when oxygen is absent (23).

On the other hand, ferritic stainless steels with little or no nickel content are, in general, highly resistant to SCC. However, once the nickel content exceeds about 1.5%, the stainless steel becomes increasingly susceptible. It is advisable to substitute ferritic for austenitic stainless steel when high tensile stresses are expected and/or environments that promote SCC are present.

Precipitation hardened martensitic stainless steels, above 1240 MPa, have exhibited cracking in salt-spray and when fully immersed in aqueous media (23). In addition, heat treated martensitic stainless steels are susceptible to SCC in moderately acidic solutions, particularly when sulfides or arsenic is present (23).

The methods used to prevent SCC cannot be generalized to include all alloys because the methods used depend on the nature of the alloy system and the environment. A method that works to control SCC for one alloy may not work for another alloy; also, a procedure that works in one environment may not be applicable in another environment for the same alloy. However, as a guideline, the most practical methods for controlling SCC susceptibility are listed below.

- (1) Lower the tensile strength, or the bending stress in some cases, to levels below which SCC does not occur.
- (2) Avoid the application of tensile stresses in the short transverse direction for aluminum alloys.
- (3) Eliminate the critical environment that promotes SCC for the given alloy.
- (4) Apply a cathodic-potential protection to reduce corrosion tendencies in aggressive environments or reduce the adsorption of surface energy reducing agents.
- (5) Addition of certain inhibitors to aqueous solutions can be effective in controlling SCC for many alloys.
- (6) Sacrificial coatings such as cadmium plating are effective for the control of SCC in aluminum alloys.
- (7) Shot peening or cold-working of steels has been used to impart residual compressive stresses in surface layers of metals to help negate tensile stresses. For example, Friske and Page (29) have demonstrated that cold-working by shot peening of 18-8 stainless steel prevented SCC in boiling MgCl_2 .

CHAPTER 9

EXPERIMENTAL

A comprehensive investigation into the corrosion behavior of materials selected for use in the construction of a weapons platform will be conducted and test results should be complete within six months. The nature of the test method and the extent of testing will depend on the proposed design and material(s) selected.

Electrochemical techniques will be used primarily to assess overall corrosion behavior in laboratory situations and concurrent visual assessment of laboratory immersion tests will be provided. Field testing will involve atmospheric exposure to a marine environment at Ft. Lauderdale, FL. A brief description of the likely experimental techniques to be used, including the necessary theoretical background, is described below.

GENERAL CORROSION BEHAVIOR

The primary objective for conducting laboratory tests is to obtain reliable corrosion rate data in short times that can be used to predict the useful lifetime of the materials. Test samples will be exposed to 3.5% NaCl and to synthetic seawater. Additional studies using other environments may be necessary because the corrosion behavior of the weapons platform may be strongly influenced by exposure to motor oil, greases, aviation gasoline, hydraulic fluid, and cleaning detergents.

Preliminary studies will involve using the polarization resistance (R_p) technique as developed by Stern and Geary (30). A Princeton Applied Research, Model 351, Corrosion Monitor will be used to make all R_p measurements. Some of the advantages of using the R_p technique are outlined below:

- (1) The potential range of interest is close to the corrosion potential and applied currents are generally smaller than the corrosion currents. Thus, the nature of the surface is not changed significantly, and results should therefore reflect the actual corrosion behavior.
- (2) The change in corrosion rate with time can be monitored without removing the sample from the test environment.
- (3) R_p measurements can be made in short times.
- (4) Small corrosion rates can be determined.

Briefly, a controlled-potential scan over a small range, typically ± 5 mV with respect to the corrosion potential, is applied to the specimen. In this potential range, the applied potential and current density are linearly related to a close approximation provided the corrosion potential is far removed from the individual reversible potentials of the anodic and cathodic reactions. Subsequently, the resulting current is plotted against the applied potential and the slope of the straight line at the corrosion potential is equal to R_p . (See Figure 5). The resultant R_p value is inversely proportional to the corrosion current. The theoretical relationship was first derived by Stern and Geary (30), as shown below:

$$\frac{\Delta E}{\Delta I} = R_p = \frac{1}{I_{\text{corr}}} \cdot \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$

or

$$I_{\text{corr}} = \frac{1}{R_p} \cdot \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$

where ΔE is the potential scan range, ΔI is the corresponding change in current, β_a and β_c are the anodic and cathodic Tafel constants respectively, and I_{corr} is the corrosion current. The calculated corrosion current is then used to determine and represent the corrosion rate in a more familiar manner, i.e., m.p.y. (milli-inches per year), using the Faraday equation

$$\frac{Q}{F} = \frac{W}{EW}$$

where Q is the number of coulombs (current x time), F is the Faraday constant (96,500 coulombs), W is the weight of the metal, and EW is the equivalent weight of the metal. The calculation of the corrosion rate using the Faraday equation in the present form may not be obvious; however, upon rearranging and substituting for the appropriate constants the following equation may be used to calculate the corrosion rate in milli-inches per year,

$$\text{MPY} = \left[\frac{EW \cdot I_{\text{corr}}}{d \cdot F \cdot A} \right] \times 1.26 \times 10^4$$

where d is the density of the metal and A is the area of exposed sample.

PITTING CORROSION BEHAVIOR

Preliminary studies will also involve a determination of the pitting susceptibility of selected materials. Electrochemical pitting tests involve the application of a cyclic potentiodynamic scan starting at the corrosion potential and moving in the positive direction. The corresponding current will at some potential increase rapidly, indicating a localized breakdown of the passive film; an example of a metal that exhibits pitting corrosion is illustrated in Figure 6 where the presence of a hysteresis loop confirms pit formation. At a preselected current, the scan direction is reversed, and during scan reversal pit formation ceases and existing pits repassivate. On the other hand, a reverse scan that traces the forward scan, as seen in Figure 7, indicates the test metal is resistant to pitting. This technique is useful for screening the resistance of an alloy to passive film breakdown. However, like many corrosion tests

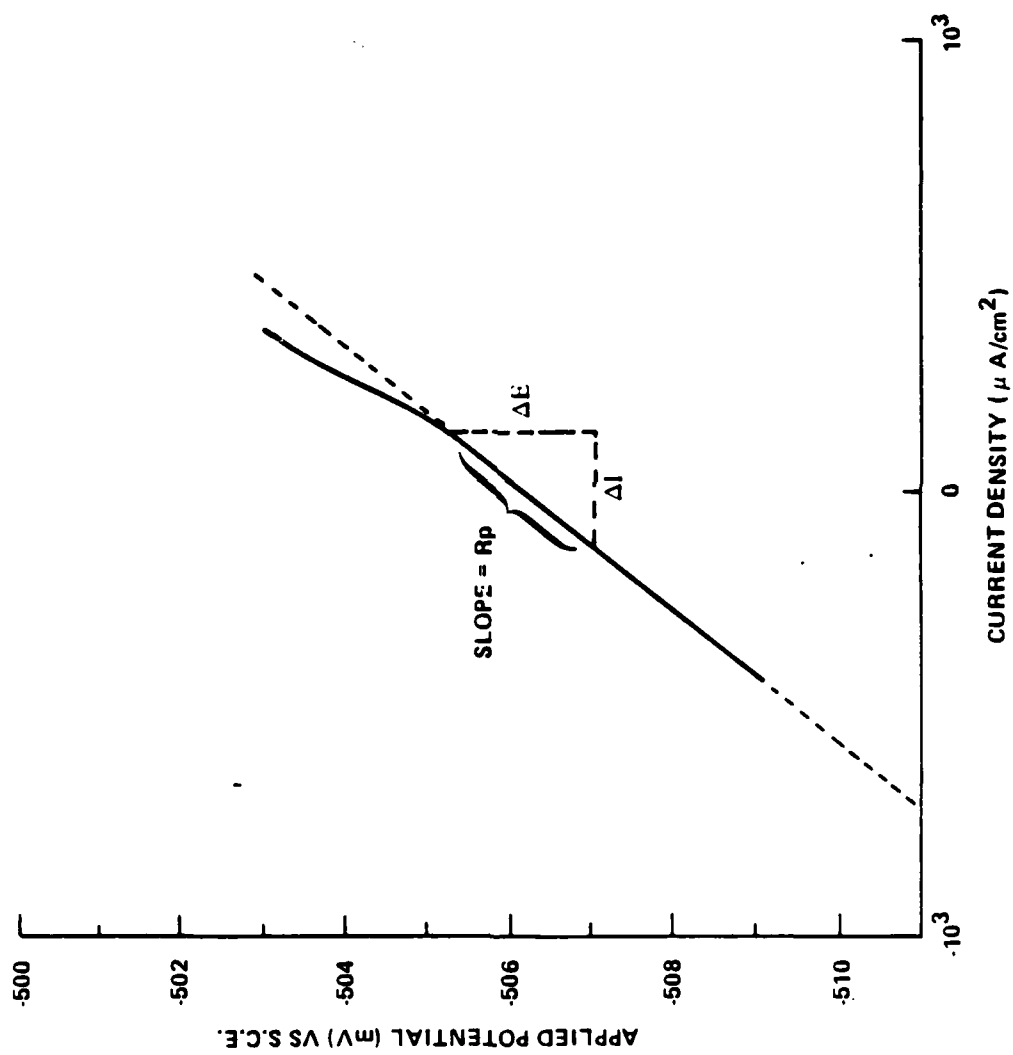


FIGURE 5. POLARIZATION RESISTANCE PLOT

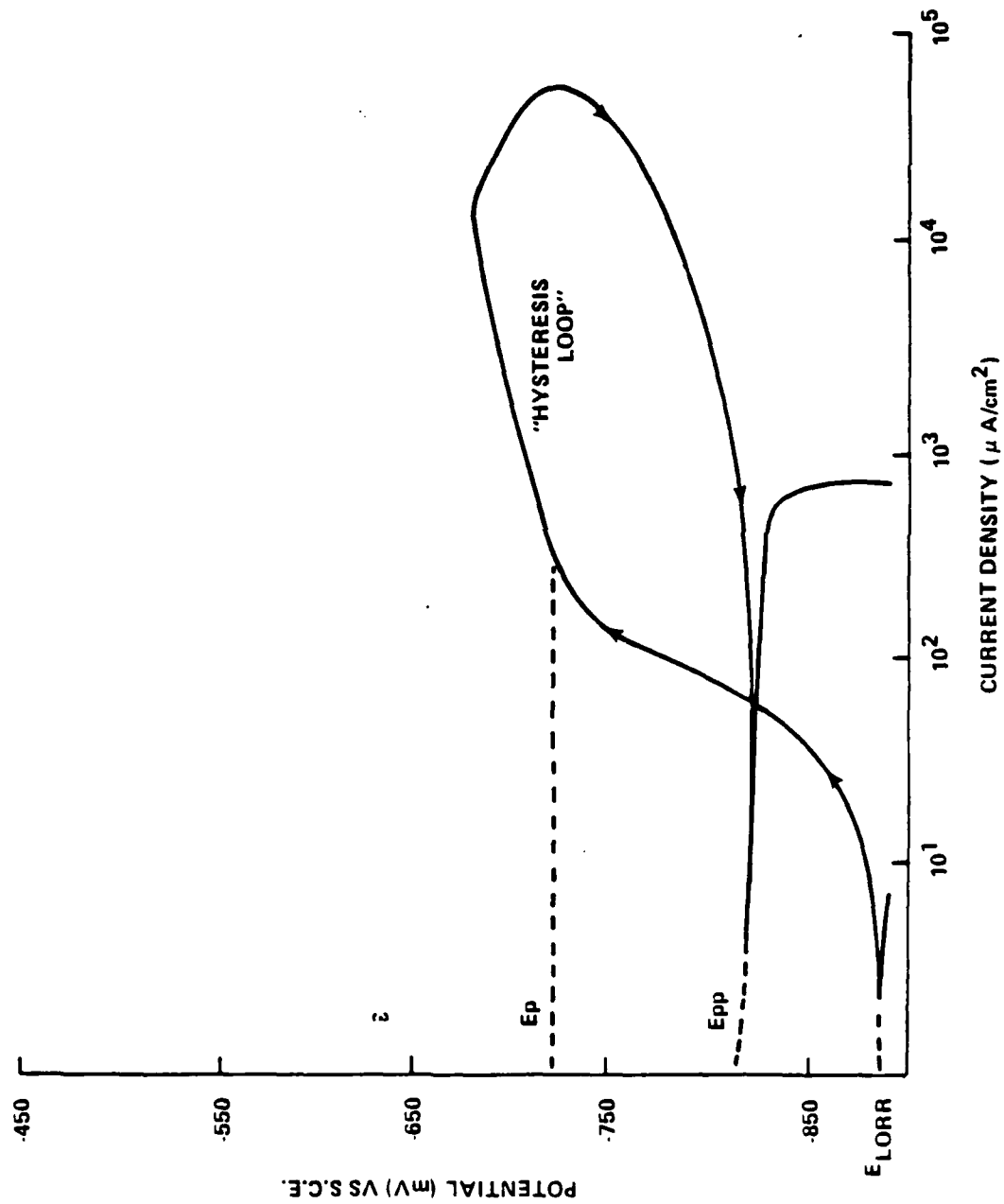
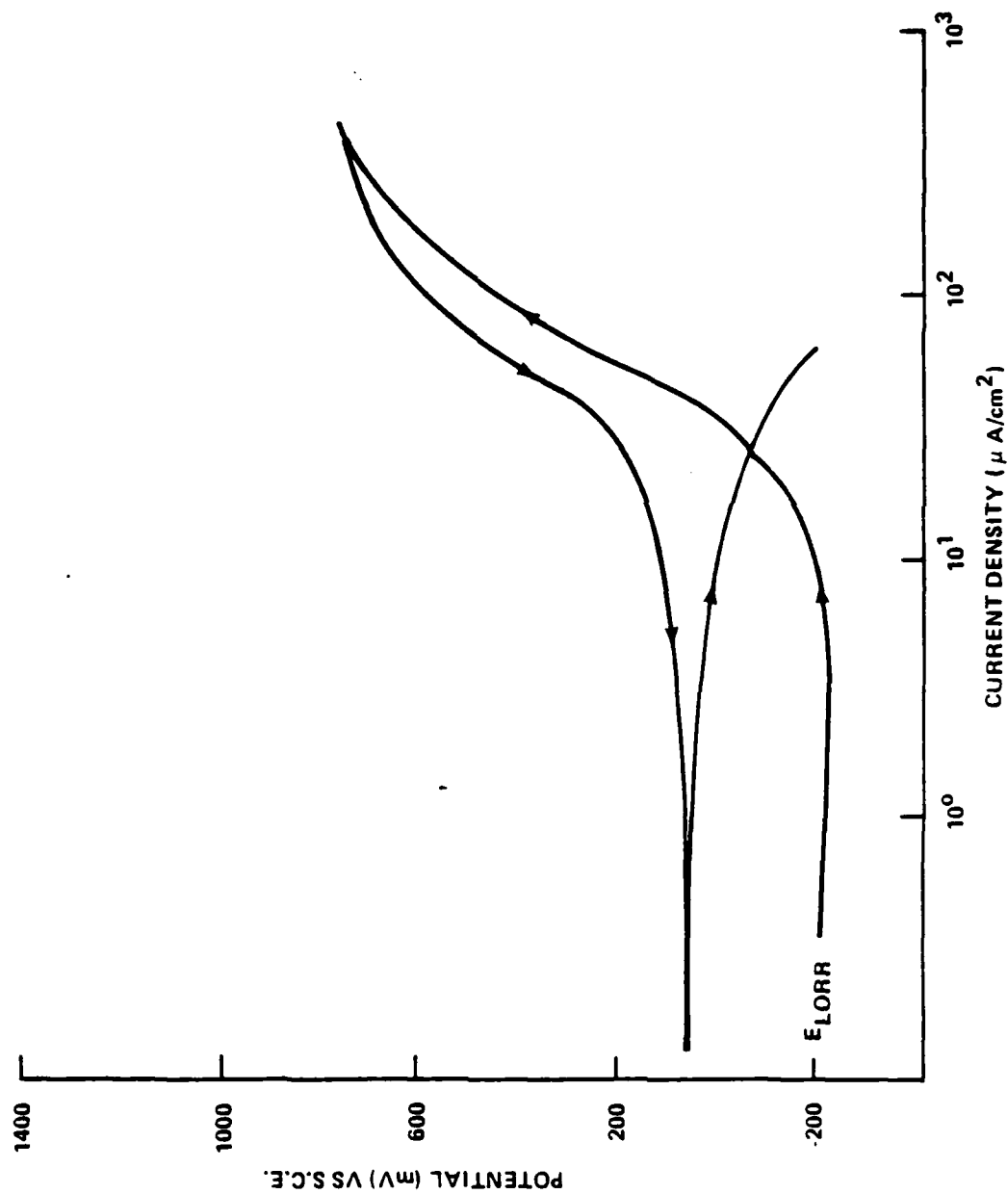


FIGURE 6. PITTING SCAN FOR ALUMINUM COMPOSITE IN 3.5% NaCl.

FIGURE 7. PITTING SCAN FOR Al-2024 IN 1N NaNO₃

designed for laboratory use, the corrosion process is accelerated and a direct comparison to the freely corroding state is sometimes difficult; therefore, some caution must be exercised when accelerated laboratory tests are analyzed. In many cases, a good correlation is obtained when comparisons can be made between accelerated laboratory tests and observations made on freely corroding specimens.

Although the use of a coated weapons platform is likely, pitting studies will help to establish the extent to which localized corrosion will occur. A painted metal will, in most cases, fail in localized areas, such as at mechanically induced defects, i.e., scratches. Localized corrosion at such defects can result in rapid attack of the exposed metal, or cathodic delamination may occur, resulting in a loss of coating adhesion in areas adjacent to the defect. The possibility that cathodic delamination may occur suggests that delamination tests should be considered. A typical cathodic delamination test can be described as follows. A defect is placed in the coating and a cathodic potential is applied in order to drive the cathodic (oxygen) reduction reaction. A sample exhibiting delamination can be recognized by a significant loss of adhesion in areas adjacent to the defect. A detailed description of the cathodic delamination process is given elsewhere (31-40). In general, coated aluminum alloys exhibit excellent resistance to cathodic delamination because the aluminum surface is inactive toward the oxygen reduction reaction, that is, the aluminum electrode is highly polarizable and results in low currents. Pryor and Keir (41) supported this conclusion with published results from their investigations on the nature of the aluminum cathode. Cathodic polarization curves for aluminum and mild steel in 1N NaCl, as seen in Figure 8, show that the aluminum electrode is highly polarizable, i.e., low currents are generated, when compared to the behavior of mild steel. Pryor and Keir (41) attribute this behavior of aluminum to an increase in the electronic resistivity of the aluminum oxide, thus effectively reducing the cathodic activity of the electrode. Coated low-alloy and mild steels often exhibit rapid cathodic delamination, as one might expect knowing that steel is nonpolarizable in aerated NaCl solution. Therefore, more care must be taken when coated steels are to be used.

CREVICE CORROSION BEHAVIOR

Crevice corrosion testing is best investigated using representative samples of the real situation and exposing these samples to the appropriate environments, such as a marine atmosphere, immersion in aviation fuel, or exposure to salt spray. Electrochemical techniques can also be utilized to study crevice corrosion; for example, the same procedure used to investigate pitting corrosion behavior can be applied to crevice studies. Crevice corrosion is often more detrimental and occurs more frequently than pitting. Therefore, when testing for pitting corrosion susceptibility, the sample must be made free of crevice sites because the preferred course of attack is usually within a crevice when present and electrochemical pitting measurements are subsequently affected. However, the same pitting technique can be used to test for crevice susceptibility in much the same manner; for example, a study conducted by Wilde (14) showed that a 30Cr-3Mo-Fe alloy free from crevice sites and exposed to 1M NaCl exhibited no signs of pitting corrosion as indicated by the absence of a hysteresis loop during the potentiodynamic scan (See Figure 9). However, when the sample contained a crevice site, a large hysteresis loop was obtained, indicating that crevice corrosion had occurred. According to Wilde (14) the

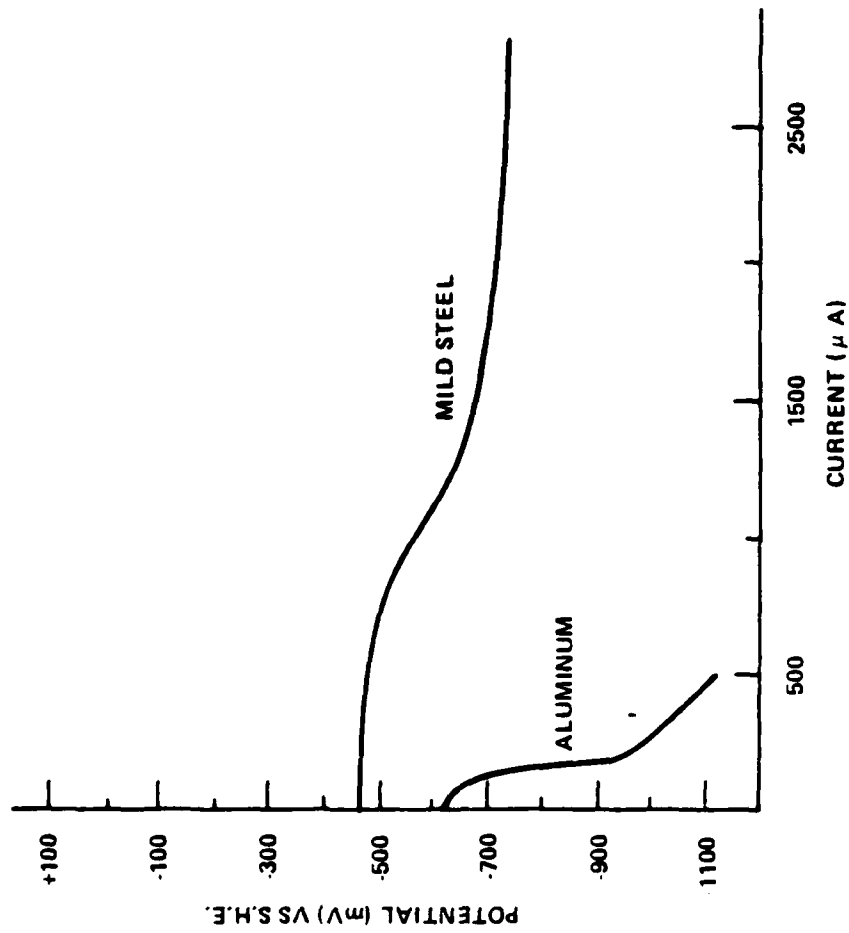


FIGURE 8. CATHODIC POLARIZATION CURVES FOR ALUMINUM AND MILD STEEL IN NaCl.

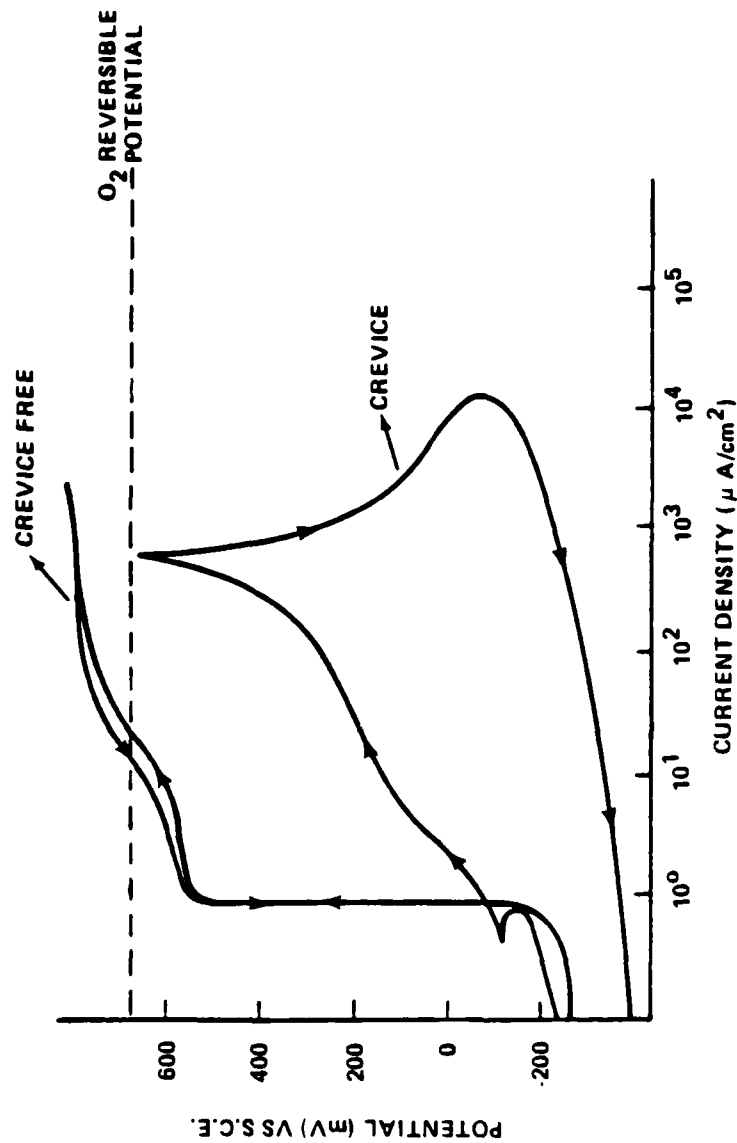


FIGURE 9. CYCLIC POTENTIODYNAMIC ANODIC POLARIZATION CURVES FOR A
30 Cr-3Mo-Fe ALLOY EXPOSED TO DE-AERATED IN NaCl @25°C.
FROM REF 14.

susceptibility of an alloy to crevice initiation may be predicted by the presence of a hysteresis loop during cyclic potential scans on specimens containing crevices. The resistance to crevice corrosion is determined by the magnitude of the area in the hysteresis loop; that is, a small area within a given hysteresis loop indicates a better resistance to crevice attack.

A sample arrangement that may be used for electrochemical studies is illustrated in Figure 10. Samples will be exposed to synthetic seawater, 3.5% NaCl, AFFF, alcohol, and other pertinent environments. A majority of crevice testing will involve marine atmospheric exposure and laboratory immersion studies using environments other than seawater. Some typical sample arrangements that may be employed can be seen in Figure 11. In addition, testing of painted samples exposed to the various environments should be examined. A multi-exposure test assembly may be constructed for immersion studies, and ASTM standard G-78 will be used as a guide. An example of a multi-sample exposure set-up can be seen in Figure 12.

GALVANIC CORROSION BEHAVIOR

Galvanic corrosion testing will be conducted only if design specifications require the use of dissimilar metals. Laboratory studies using techniques to monitor the galvanic currents generated by coupled metals and field exposure to marine environments will be conducted as the need arises. Galvanic corrosion measurements will involve monitoring the galvanic current generated by the dissimilar couple using a zero-impedance ammeter. The experimental samples will be appropriately scaled to represent the actual cathode-to-anode area ratios that are to be expected from a given platform design. Individual galvanic couples will be electrochemically tested in synthetic seawater and exposed to a salt-fog environment for visual inspection. In the event that dissimilar metals are needed for the construction of a weapons platform, the potential dangers arising from galvanic attack can be minimized by using protective coatings, provided all portions of the structure are coated and no breakdown of the paint occurs in areas where the active element of the couple is located. Therefore, proper galvanic testing requires examining the behavior of coated-coupled metals.

STRESS CORROSION CRACKING

A large number of experimental specimens are currently used to evaluate SCC. Specimens can be classified into three groups: smooth, precracked, and tensile. (See Figure 13). Certain smooth-type specimens, such as the U-bend specimen, can only be used for qualitative evaluation and useful only for determining the SCC susceptibility for given alloys and environments. However, smooth-type specimens such as the C-ring specimen can be used to quantify the stress, thus permitting a calculation of threshold stresses below which SCC will not occur. The second class of SCC specimens involves the use of precracked test samples. These specimens are important because of the possibility of placing a structure into service with crack-like flaws; therefore, the testing of precracked samples is logical. A small tensile specimen is generally used in the third class of SCC test specimens. The tensile specimen is used in a constant strain rate or slow strain rate test where the ductility and fracture strength of the sample is affected by the nature of SCC and the extent to which cracking has occurred prior to fracture failure.

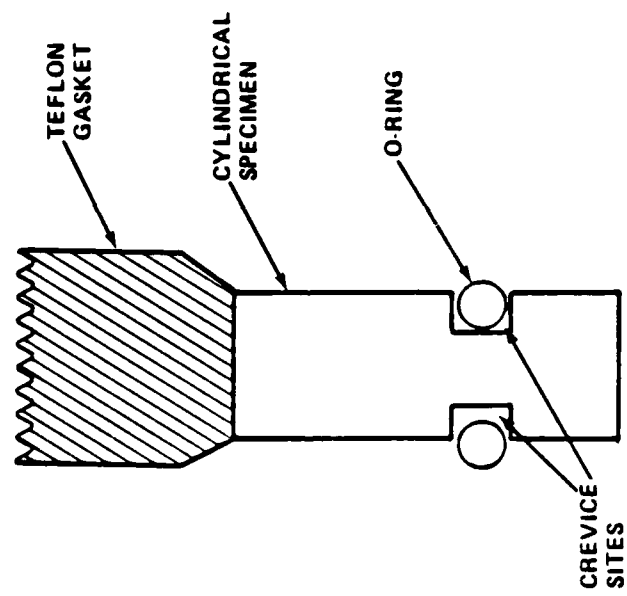


FIGURE 10. ELECTROCHEMICAL CREVICE TEST SPECIMEN

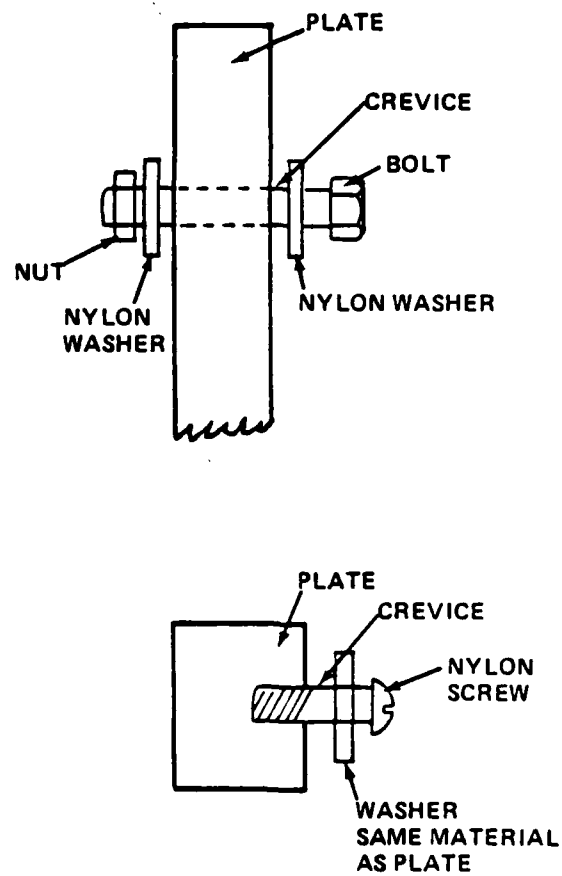


FIGURE 11. CREVICE TEST SAMPLES

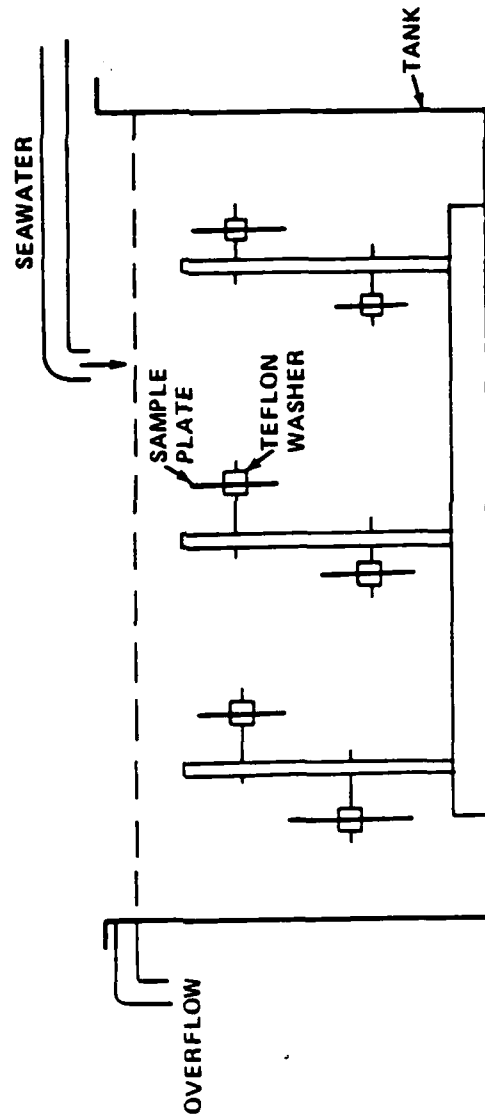


FIGURE 12. MULTI-CREVICE TEST SET-UP

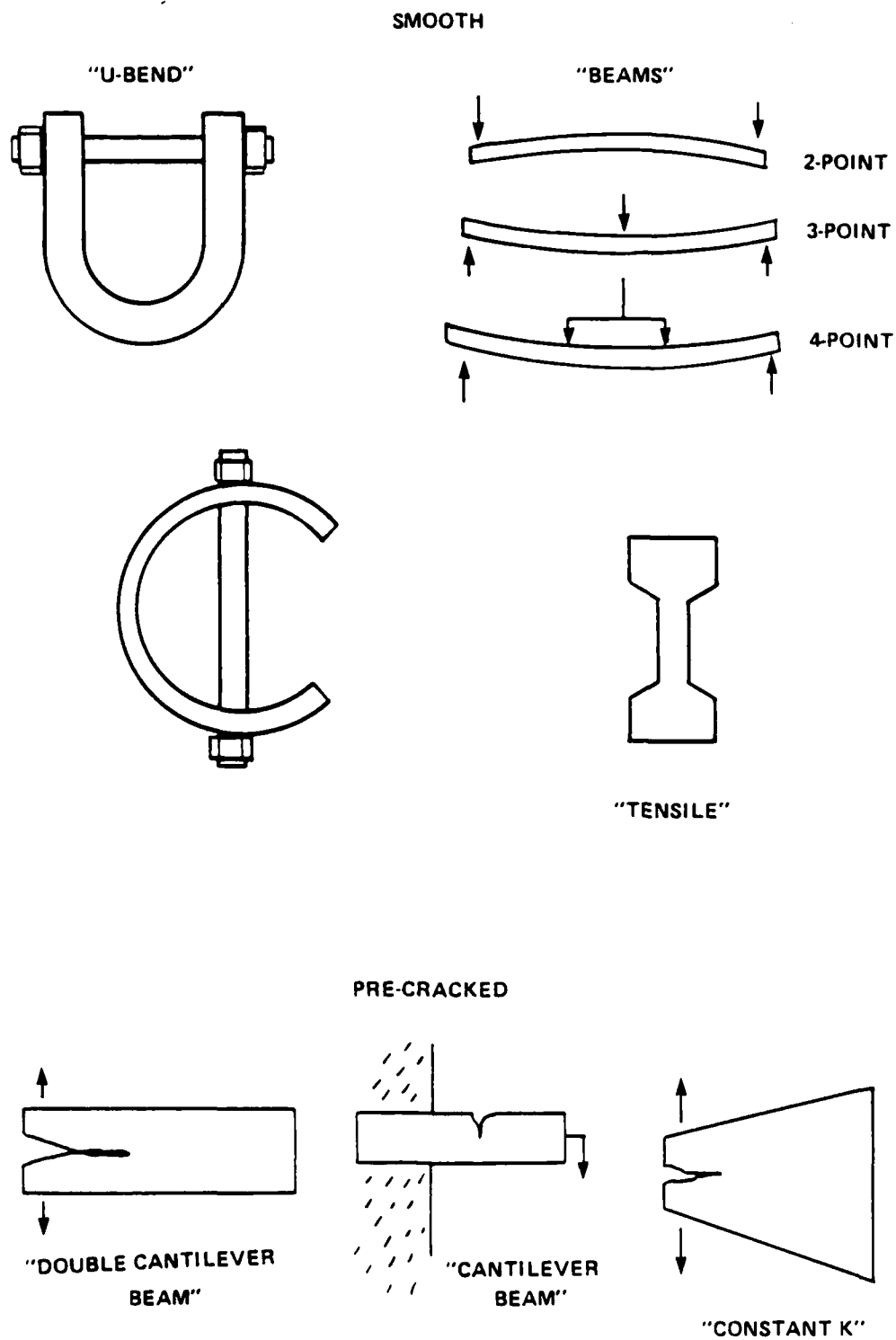


FIGURE 13. STRESS CORROSION CRACKING TEST SPECIMENS

Preliminary SCC testing on materials considered for use in a weapons platform will be conducted using smooth test specimens, e.g., U-bend specimens. Smooth specimens will be used initially to determine the SCC susceptibility of selected materials in appropriate environments. For engineering applications, an alloy that exhibits SCC in the qualitative tests and remains a candidate material should be tested using quantifiable smooth specimens in order to determine threshold stress values.

Materials that are known to exhibit SCC in environments to which the weapons platform is expected to experience should be avoided at all costs. Examples of those alloys that are susceptible to SCC and the environments that are conducive to SCC were discussed in Chapter 8 and appropriate references were cited. Alloys that are highly susceptible to SCC are not recommended for use in the construction of a weapons platform unless tensile stresses can be made lower than threshold stresses and protection from the environment is guaranteed.

PAINT PROTECTION

U.S. Naval requirements specify that the weapons platform must conform to paint regulations; specifications are outlined and certain guidelines must be followed. The required use of protective coatings suggests that perhaps the main thrust of corrosion research should be on the behavior of a coated weapons platform. Careful attention must be directed toward the design of a new platform, particularly when new materials are selected, to ensure that application of protective coatings remains practical. In addition, selection of new materials may change the effectiveness of established methods of surface pretreatment; for example, commonly used surface pretreatment procedures involve sand blasting or shot blasting to remove mill scale, old paint, or rust, and to roughen the surface to enhance coating adhesion. This approach works well for most steel structures; however, problems may develop when aluminum alloys are used because they are inherently soft and particles are easily embedded into the aluminum surface. The embedding of foreign particles into a metal surface may set up local galvanic cells or coating adhesion may be seriously affected. Pumice may be substituted for sand or steel grit for abrasive blasting of aluminum. All metals require some form of surface pretreatment prior to painting because the protective nature of a coating is only as good as the surface to which it is applied. Therefore, when new materials are selected, the designer must recognize the need to successfully apply protective coatings.

To ensure an accurate appraisal of newly selected materials, an understanding of the corrosion behavior of painted specimens is imperative and coated test samples must be prepared according to established standards. Atmospheric exposure to marine environments must be conducted on samples with and without defects to test coating adhesion; in addition, immersion studies need to be initiated where samples are exposed to salt water, detergents, AFFF, aviation fuels, alcohols, and hydraulic fluids. All atmospheric and immersion exposure samples should be prepared under identical conditions in order to eliminate as many variables as possible. Additional studies should involve the study of samples exposed to salt-spray conditions of alternating wet and dry cycles.

CHAPTER 10

CONCLUSION

The need to understand in advance the nature of corrosion and to identify the more serious corrosion problem areas requires no justification, especially when a new structural design is to be considered. The purpose of this report is to provide an introduction to the nature of specific types of corrosion and to highlight potential problem areas that could adversely affect the operation of a new generation of weapons platforms.

The most important types of corrosion failures that require careful attention include pitting and crevice corrosion, galvanic corrosion, and stress corrosion cracking. All potential forms of corrosion are greatly reduced when protective coatings are employed; however, the potential for underfilm attack is always a possibility, especially in the presence of coating defects. A particularly dangerous situation may develop when cathodic protection is used to protect a coated substrate; the application of an impressed cathodic current may result in cathodic delamination of the coating in areas adjacent to a defect, resulting in significant loss of adhesion. Therefore, a comprehensive corrosion investigation must include the study of coated materials.

Replacement of the existing weapons platform with a reliable substitute is the primary goal of this project. Design priorities must provide for significant weight reduction, structural integrity, and cost savings. Preliminary corrosion studies should help to ensure that the structural integrity will not be compromised. The need to reduce the weight of the platform suggests that new materials are required. Aluminum alloys are the most likely replacement candidates for the present steel platform; aluminum alloys are lightweight, inexpensive, easy to fabricate, and exhibit good corrosion resistance. The use of high cost metal composites is less desirable because of limited availability and difficulty of fabrication. In addition, other alloys such as stainless steel, although highly corrosion resistant, offers little or no weight reduction. The use of expensive nickel, chromium, and titanium alloys is likewise undesirable. The selection of aluminum alloys to replace steel requires some added care, and therefore a number of examples related to the corrosion behavior of aluminum have been cited in this report.

The number of potential problem areas detrimental to the structural integrity of aluminum alloys must be realized when exposure to marine environments is anticipated. A summary of some of the more important concerns is given below.

- (1) Aluminum should not come in contact with nickel, titanium, copper, or stainless steel alloys.

- (2) A tough nonporous barrier coating is needed to protect aluminum against corrosion and to enhance paint adhesion.
- (3) Aluminum alloys containing zinc or copper are brittle, which makes them highly susceptible to SCC. Therefore, the use of these alloys should be avoided, or the application of large tensile stresses in the short transverse direction must be kept low.
- (4) In general, aluminum can be painted with little difficulty; however, the type of surface pretreatment needs to be carefully examined.
- (5) Paints that contain heavy metals such as lead should be avoided because of the possibility of establishing local galvanic cells.

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R32 (W. Lee)	1
E31 (GIDEP Office)	1
E53 (GIDEP Office)	1
E231	9
E232	3
G61 (E.P. Lefave)	1
R35 (K.A. Musselman)	1
R35 (J. Hall)	1
E22 (D. B. Johnston)	1

END

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DTIC